REMARKS

The abstract and specification have been amended in order to correct the numerous grammatical and idiomatic errors contained therein. No new matter has been added.

In order to expedite the prosecution of the present application and to more particularly point out and distinctly claim the subject matter which Applicants regard as the invention, non-elected Claim 1 and Claims 2-4 have been canceled without prejudice. Newly presented Claims 5-15 more particularly point out and distinctly claim the subject matter which Applicants regard as the invention. No new matter has been added.

Claims 2-4 have been rejected under 35 USC 112, second paragraph, as being indefinite and Claim 4 has been objected to under 37 CFR 1.75(e). It is respectfully submitted that the currently presented claims are cured of all formal defects.

Claims 2-4 have been rejected under 35 USC 103(a) as being unpatentable over Sudhakar et al. Applicants respectfully traverse this ground of rejection and urge reconsideration in light of the following comments.

The presently claimed invention is directed to a method of hydrocracking a heavy oil comprising the steps of contacting the heavy oil with a catalyst comprising iron and active carbon having an MCH conversion rate of 40-80%, specific surface area of 600-1,000 m^2/g, pore volume of 0.5-1.4 cm^3/g, 2-50 nm mesopore volume of not less than 60% and average pore diameter of 3-6 nm, the iron being carried on the active carbon in an amount of 1-20 wt.% with respect to the active carbon.

As discussed in the present specification, the presently claimed invention is characterized by the hydrocracking of heavy oils which can contain large amounts of contaminants such as heavy metals and asphaltene. The present invention is based on the discovery of a catalyst mainly containing iron

and active carbon having an MCH conversion rate of 40-80%, specific surface area of 600-1,000 m^2/g, pore volume of 0.5-1.4 cm^3/g, 2-50 nm mesopore volume of not less than 60% and average pore diameter of 3-6 nm, with the iron being carried on the active carbon in an amount of 1-20 wt.% with respect to the active carbon, can be used in the hydrocracking of heavy oils with unexpected benefits of preventing side-production of cokes and remove heavy metals, such as nickel and/or vanadium, and asphaltene. It is respectfully submitted that the Sudhakar et al reference does not disclose the presently claimed invention.

The Sudhakar et al reference discloses a process for pretreatment of a hydrocarbon oil feed containing sulfur and nitrogen compounds and aromatics prior to hydrocracking or fluid catalytic cracking. The process comprises a step of contacting the feed stock with a sulfided catalyst comprising a metal of non-noble Group VIII and Group VI B, and, optionally one or more elements selected from Group III A and Group V A of the periodic table on a carbon support consisting essentially of activated carbon and, optionally, on a carbon support treated with phosphorus.

Although Sudhakar et al discloses in column 5, lines 53-61, that the charged hydrocarbons include hydrocarbon oil feeds generally heavier than kerosene, including, but not limited to all atmospheric gas oils, all vacuum gas oils, residua and whole crude oils, heavy naphtha and may also be derived from petroleum, coal, shell, tar sands, oil sands and other synthetic fuels, the only examples in this reference use gas oils. Gas oils inherently do not include either nickel or vanadium. In this reference, the gas oil is modified to remove matters which cause the side-production of coke in a step of hydrodearomatization, which is referred to in column 5, line 55 of this reference. If heavy oils were treated according to the process of the examples of this reference, coke would be produced as a side-product. Additionally, the

catalyst in this reference can carry a metal of both Group VIII and a metal of Group VI B. There is no specific disclosure that anything advantageous would occur by using iron as the catalytic metal. Lastly, this reference fails to disclose any problems resulting from impurities such as heavy metals, nickel, vanadium or asphaltene because gas oils do not contain these impurities.

In contrast to the Sudhakar et al reference, the presently claimed invention is concerned with the hydrocracking of a heavy oil. As a result of the inventive process of the present invention, the unexpected benefits of the prevention of the side-production of cokes and the removal of heavy metals, nickel and/or vanadium and/or asphaltene can be accomplished. In the catalytic composition of the present invention, iron is an essential ingredient and other metals can in fact be excluded therefrom. Moreover, the catalyst of the present invention is required to have an MCH conversion ratio of 40-80% and other specified physical properties. With the present invention, heavy oil can be efficiently cracked while coke generation suppressed. Additionally, heavy metals are also removed.

The heavy oil of the present invention has a higher boiling point than that of the Sudhakar et al reference in that it includes 70-94% of fractions having a boiling point higher than 525°C. In contrast thereto, in the examples of Sudhakar et al, the gas oil fractions have boiling points of from 126-413°C. As pointed out above, only gas oil is specifically treated in the reference. It is well known to one of ordinary skill in the art that heavy oil cannot be treated in the same fashion as gas oil. Heavy oils treated according to the process of Sudhakar et al would generate a significant amount of coke to clog piping and cause other problems. Additionally, this reference has no mention of the problems caused by heavy metals as impurities and therefore provides no motivation to remove these impurities. Enclosed

herewith for the Examiner's benefit is a table which illustrates the differences between the present invention and the disclosure of Sudhakar et al.

In order to further illustrate the difference between heavy oil and gas oil, Applicants are enclosing herewith three references. The references are listed below with a synopsis of the disclosure of these references.

D1: PETROLEUM REFINING INDUSTRY Energy Saving and Environmental Control, M. Sittig, NOYES DATA CORPORATION, 1978

D2: PERRY'S CHEMICAL ENGINEER'S HANDBOOK, 6^{th} Edition, R. H. Perry, D. Green, McGRAW-HILL International Editions

D3: PETROLEUM REFINERY ENGINEERING, 4^{th} Edition, W. L. Nelson, McGRAW-HILL Book Company

D1 shows, in Figure 12, a general material flow of a Petroleum Refinery in the form of a Process Flow Diagram. Crude oil is distilled through Atmospheric Crude Topping Unit (Topping still, Topper) and Vacuum Distillation Unit into fractions having different boiling points. Downstream processes remove impurities such as sulfur, nitrogen and heavy metals and specify final products.

It is noted from D1 that crude oil is fractionated to heavy oil such as reduced crude and residium and then gas oil such as heavy gas oil.

D2 shows, Figure 13-76, details of distillation steps, indicating boiling points of fractions. The boiling point is higher in order of Gas < Naphtha < Kerosene < Diesel < Atmospheric Gas Oil < Light Vacuum Gas Oil < Heavy VGO < Residue. The viscosity also increases in the same order. Treatment gets more difficult in the same order.

It is known to a person skilled in the art that Kerosene, Diesel and Atmospheric Gas Oil are gas oil disclosed in the Sudhakar et al reference. In the present invention, Reduced Crude after distillation at the atmospheric pressure is

treated. It includes principally a Residue having a boiling point of 525°C or higher and includes V and Ni.

In order to provide support for Applicants' position that coke and other impurities are contained in crude oil, Applicants are enclosing herewith the references cited below and a synopsis of each reference.

D4: International Petroleum Encyclopedia, 1979, pp 286-287

D5: Modern Petroleum Technology 4th Edition, The Institute of Petroleum, Applied Science Publishers LTD

Crude oil contains undesirable impurities such as sulfur, nitrogen and heavy metals. High boiling point fractions contain these impurities in a larger amount than lower boiling point fractions.

D4, Table 1, shows fractions obtained by distilling Isthmus export crude, crude oil. In the table bridging between pages 286 and 287, fractions are listed in order of boiling points, the lowest being the first. It is noted that Light gas oil and Heavy gas oil, called also Atmospheric gas oil, include 0.1 ppm or smaller of Ni and 0.5 ppm or small of V. The Residue includes 13.0 ppm of Ni and 120 ppm of V. It is evident that the heavy oil to treat in the invention includes most of the heavy metals from crude oil.

D5 shows, on page 198, metals contained in crude oil. Vanadium and Nickel are stable in crude oil and contained in porphyrin, the principal structure of the Residue. Those having a low molecular weight and being volatile are contained just in a small amount in a Vacuum Gas Oil fraction. The porphyrin including Vanadium and/or Nickel very often causes coking or sludge, clogging pipes or heat exchangers, forming poison to the catalyst. So important problems are this way raised in petroleum refining. It is important to the specification of the final product.

D1 shows, in Figure 12, that fractions downstream from distillation are different from one another in view of easiness of treatment and amounts of impurities. A person skilled in the art may choose any fraction for his purpose from the viewpoint of impurities.

For the reasons advanced above, it is respectfully submitted that the currently claimed invention clearly is patentably distinguishable over the prior art cited by the Examiner. Reconsideration of the present application and the passing of it to issue is respectfully solicited.

Respectfully submitted,

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Encl: Marked-Up Amended Abstract and Specification
Substitute Abstract
Table
References D1-D5
Information Disclosure Statement and
Petition for Consideration including
Form PTO-1449 and one copy of each
reference listed thereon
Postal Card

136.0112

CATALYST FOR HYDROCRACKING OF HEAVY OILS AND METHOD OF HYDROCRACKING HEAVY OILS

Abstract

A catalyst for the hydrocracking of heavy oils contains iron and active carbon having an MCH conversion rate of 40-80%, a specific surface area of 600-1000 m^2/g of, a pore volume of 0.5 to 1.4 cm^3/g, 2-50 nanometers' mesopore volume of not less than 60% and an average pore diameter of 3-6 nanometers, the iron being carried on the active carbon in an amount of 1 to 20 wt.% to the active carbon. The hydrocracking process using the catalyst includes a first step of conducting hydrocracking at a temperature within the range of 360-450°C at a hydrogen partial pressure of 2-14 MPaG and a second step of conducting hydrocracking at a temperature within the range of 400-480°C at a hydrogen partial pressure of 2-18 MPaG, which can suppress the generation of coke and remove, in a high efficiency, heavy metals such as Ni and V, asphaltene, residual carbon, sulfur and nitrogen from the heavy oils.

B1

TABLE

	The invention	US 5,529,968
	Claim 1	Claims and description
	: iron and activated carbon	: carbon treated with phosphorus and metals
MCH conversion rate	: 40-80%	: no disclosure
Specific surface area	: 600-1000m^2/g	:100-2000m^2/g
Pore volume	: 0.5-1.4cm^3/g	: at least 0.3cc/g
Mesopore volume	: 60% or larger (2-50nm)	: 20-80% : (20-500 A diameter) : (2-50 nm diameter)
Average pore diameter	: 3-6 nm	: 12-100 A : (1.2-10 nm)
Iron content	: 1-20 wt%	:
Metal contents		: 0.1-15 wt% : (one of Fe, Co and Ni) : 1-50 wt% : (W) : 1-20 wt% : (Mo or Cr)

1A=10^{-8}cm=0.1nm
1nm:10^{-9}m=10^{-7}cm
1psi=6894.76Pa

IN THE ABSTRACT

Please amend the abstract as follows.

CATALYST FOR HYDROCRACKING OF HEAVY OILS
AND METHOD OF HYDROCRACKING HEAVY OILS

Abstract

A catalyst for the hydrocracking of heavy oils ~~comprises~~contains iron and active carbon having an MCH conversion rate of 40-80%, a specific surface area of 600-1000 m^2/g of, a pore volume of 0.5 to 1.4 cm^3/g, 2-50 nanometers' mesopore volume of not less than 60% and ~~the~~an average pore diameter of 3-6 nanometers, the iron being carried on the active carbon in an amount of 1 to 20 wt.% to the active carbon. The hydrocracking process ~~by~~using the catalyst includes ~~the~~a first step of conducting hydrocracking at a temperature within the range of 360-450°C at a hydrogen partial pressure of 2-14 MPaG and ~~the~~a second step of conducting hydrocracking at a temperature within the range of 400-480°C at a hydrogen partial pressure of 2-18 MPaG, which can suppress the generation of coke and remove, in a high efficiency, heavy metals such as Ni and V, asphaltene, residual carbon, sulfur and nitrogen from the heavy oils.

IN THE SPECIFICATION

Please amend the Background of the Invention section, beginning on page 1 and ending on page 8, as follows.

~~Background of the Invention~~

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method of hydrocracking heavy oils or extraheavy oils with the generation of coke being suppressed. More specifically, the present invention relates to a method of hydrocracking heavy oils or the like wherein the generation of coke is suppressed in the presence of pressurized hydrogen and a catalyst comprising active carbon having ~~a~~specific properties and comprising iron carried on the active carbon, and heavy metals such as Ni and V, asphaltene, residual carbon, sulfur, nitrogen and the like in the heavy oil or e~~s~~xtraheavy oil, are removed by cracking and subjected to a heat treatment.

Description of the Related Art

Recently, as the world-wide trend in the petroleum refinery industry, the proportion in production of light-weight products is increasing. Accordingly, it is becoming more and more important, from the standpoint of effective utilization of resources, that heavy oils or extraheavy oils such as atmospheric distillation-residual oils, vacuum distillation-residual oils, catalytically cracked residual oils, oil sand oils and coal-liquefied oils and the like, which remain after removing valuable light-weight fractions, can be hydrocracked and further converted into useful intermediate fractions.

There have been a number of reports about the hydrocracking of heavy oils by using catalysts. As one example of upgrading heavy oils by using catalysts containing active carbon having specific properties with a metal carried thereon, US-A 5,358,634 and US-A 5,364,524 have been proposed.

In US-A 5,358,634, a process of hydrocracking heavy hydrocarbon oils by using an active carbon catalyst

having specific properties is disclosed. This is a method of cracking a heavy hydrocarbon oil which contains no less than 70% of a heavy oil content having ~~the~~a boiling point of not lower than 343°C in a fixed-bed reactor. The reference suggests that, according to the method, under the existence of active carbon having at least 0.2 cc/g of pore volume and at least 50 m^2/g of surface area of ~~the~~a pore distribution range of 10-40 nanometers, the average pore diameter being 4 to 5.4 nanometers, the heavy metal (Ni and V) removal rate is at least 59%, the desulfurization rate is at least 9.5%, the residual carbon decomposition rate is at least 13.5% and the removal rate of asphaltene defined as a content insoluble to pentane is at least 10%.

US-A 5,364,524 discloses a process of hydrocracking a heavier oil. This is a method of hydrocracking a heavy hydrocarbon oil which contains no less than 97% of a heavy oil content having ~~the~~a boiling point of not lower than 343°C in a fixed-bed reactor. The reference suggests that, according to the method, under the existence of a catalyst in which Mo (or W) and Co (or Ni) are carried on an active carbon carrier having properties including at least 0.2 cc/g of pore volume and at least 50 m^2/g of surface ~~are of the~~has a pore distribution range of 10-40 nanometers, the average pore diameter being 4 to 6 nanometers, at least 23% of Ni and V can be removed.

These prior arts are clearly different from the present invention which will be described below, in terms of the properties of the catalyst, the types of metals carried on the catalyst, the type of the reactor, as well as the heavy metal removal rate and the residual carbon decomposition rate.

On the other hand, the applicant of the present invention has proposed in JP-A 6-165935 a method in which hydrocracking with a relatively small amount of hydrogen consumption is made possible by using, as the hydrocracking catalyst for heavy oils, a catalyst in which metal active components such as ~~N~~nickel and iron selected from ~~the VIII~~group VIII in the periodic table are carried on active carbon produced from brown coal as a carrier. However, according to this method, as heavy oils are hydrocrack~~ing~~ed at only one stage in the process, it is difficult to reduce the amount to be used of the catalyst and suppress the generation of coke at a high conversion rate.

In addition, the applicant of the present invention has proposed in JP-A 9-235569 a method of hydrogenating heavy oils at two stages as one of the improved versions of the technique belonging to catalytic hydrocracking. In order to carry out the hydrocracking of heavy oils ~~at~~in two stages, this method comprises: ~~the~~a first step of adsorbing a coke precursor and coke into a coke adsorbent to remove them, the coke precursor and the coke being obtained by carrying out a thermal decomposition of the heavy oil under the existence of 2 to 10 wt.% of the coke adsorbent to the feedstock oil and hydrogen; and ~~the~~a second step of carrying out a thermal decomposition of the substantially whole amount of the thermally decomposed oil obtained by the first step from which the coke precursor and the coke hav~~ing~~e been removed, under the presence of hydrogen, iron compounds and active carbon having properties such as ~~the~~a MCH conversion rate of 45-85%, specific surface area of 800-1000 m^2/g, pore volume of 0.7 to 1.4 cm^3/g, mesopore (2-50 nanometers) volume of not less than 70% and ~~the~~average pore diameter

of 3-6 nanometers. The coke adsorbent of the first step comprises: at least one carbon material selected from the group consisting of brown coal, brown coal char, petroleum cokes, active carbon, carbon black and graphite; and at least one member of iron compounds selected from the group consisting of iron sulfide, iron oxide and natural pyrite. At the first step, the carbon material and the iron compounds are present in a simply mixed state in the heavy oil. The iron compound of the second step includes at least one member of compounds selected from the group consisting of iron sulfide, iron oxide and natural pyrite. At the second step, the active carbon and the iron compounds in the thermally decomposed oil are present in a simply mixed state. However, in the method of simply mixing the carbon material and the iron compounds in the hydrogenation of heavy oils at two stages as disclosed in JP-A 9-235569, since the density of the carbon material and that of the iron compound differ from each other and, as the reaction proceeds, each density varies according to the amount of coke precipitated and heavy metals deposited on the carbon material and the iron compound, selection of the conditions in fluidization operation using gases and liquids for homogeneously dispersing the catalyst becomes complicated and difficult.

In the method in which the carbon material and the iron compounds are present in heavy oils in a simply mixed state, if the conditions in fluidization operation are selected such that the catalysts are homogeneously dispersed in the reactor, a suspension type or slurry bed may be selected and the catalysts flow out of the reactor with gases and cracked oils. In a case in which there is a preposition that catalysts are disposed of after use,

such a suspension type may not be a problem. However, if re-use of the catalysts which still keeps a sufficient level of activity is intended, it is necessary to separate the catalysts which have flowed out of the reactor from the cracked oils and to recycle the separated catalysts to the reactor, which makes the process complicated.

In the RFCC processes for increasing production of the gasoline fraction and the process of hydrodesulfurizing feedstock to be supplied to the RFCC processes, when a feedstock which contains a relatively high amount of residual carbon content and metals such as Ni and V is supplied, some of ~~such~~the residual carbon and metals poison~~s~~ the catalyst and deterioration of the catalysts occurs, although the degree of the deterioration depends on the feedstock to be supplied. Conventionally, in hydrodesulfurizing, a step of removing Ni and V, in what is called a guard reactor, is provided prior to the hydrodesulfurization in order to reduce deterioration of the catalysts due to deposition of Ni and V and precipitation of coke on the catalysts. In the case of the catalyst used here, the pores of the alumina carrier ~~as a carrier is~~are made larger so that a relatively large molecule of asphaltene, which contains Ni and V, be ~~dicomosed~~decomposed and thus Ni and V be removed. However, the catalytic ability is not sufficient and complicated operations including frequent switching of the reactor, constant supply/removal of the catalysts and the like are frequently necessitated, in order to replace the catalysts which have been deactivated due to precipitated coke and deteriorated due to deposition of Ni and V thereon.

Lillian A. Rankel, Energy & Fuels 1993, 7, 937-942 discloses properties of a catalyst containing active carbon with metals carried thereon, i.e., a CoMo/carbon catalyst, whose properties are shown in Referential Example 1 described hereinafter. In this catalyst, the V removal rate is equal as compared with the catalyst of the present invention, but the conversion rate is suppressed at a low level in order to prevent generation of coke. In addition, the Ni removal rate, the desulfurization rate and the residual carbon removal rate thereof are also suppressed at a relatively low level. Accordingly, it is obvious that the performances of the catalyst of the present invention are more excellent than those of the aforementioned catalyst.

Further, it is difficult to process used alumina catalysts on which Ni and V have been accumulated. Expecting that, in the future, crude oil will probably become heavier, that is, contain more heavy metals, more residual carbon and the like, when materials containing more heavy metals, asphaltene and residual carbon, etc. will be supplied under such a circumstance, it has been desired that a technique which enables, with a high efficiency, removal of heavy metals from the feedstock and decomposition of asphaltene, residual carbon etc. in the aforementioned process is developed.

In short, excellent techniques for processing extraheavy oils which contain a significantly large amount of impurities, such as heavy metals (Ni and V), asphaltene and residual carbon, will become essential in future.

Catalysts can be used in a fixed-bed. However, when extraheavy oils are processed, especially, since heavy metals like Ni and V as impurities contained at a high

percentage in the extraheavy oils are more likely to deposit on the catalysts and cokes generated from asphaltene and residual carbon are more likely to precipitate, it is very important that the catalysts are homogeneously dispersed in the reactor and the fluid state thereof is sufficiently maintained so that the reaction temperature be evenly maintained and partial retention of the deposits and precipitates be prevented.

Please amend the paragraphs beginning on page 8, line 12, and ending on page 9, line 22 as follows.

The inventors of the present invention have, as a result of assiduous study for solving the problems of the prior art, discovered that, by using a catalyst in which iron is carried on active carbon, the catalyst can be effectively used until the catalyst loses its activity without allowing the catalyst to flow out of the reactor and the reaction temperature can be evenly maintained and partial retention of the deposits and precipitates can be prevented because conditions in fluidization operation by gases and liquids can be easily selected and homogeneous dispersion of the catalyst and a fluid state can be sufficiently maintained, thereby allowing the catalyst to demonstrate its full capacity as a catalyst in achieving suppression of coke-generation and removing heavy metals. The invention has been completed on the basis of these discoveries.

That is, the present invention discloses a catalyst for the hydrocracking of heavy oils, comprising iron and active carbon having properties of an MCH conversion rate of 40-80%, a specific surface area of 600-1000 m^2/g, a pore volume of 0.5 to 1.4 cm^3/g, a 2-50 nanometers'

mesopore volume of not less than 60% and ~~the~~an average pore diameter of 3-6 nanometers, the iron being carried on the active carbon in an amount of 1-20 wt.% with respect to the active carbon.

In addition, the present invention discloses a method of hydrocracking heavy oils and the like by using the aforementioned catalyst, which comprises the first step of conducting hydrocracking at a temperature within the range of 360-450°C at a hydrogen partial pressure of 2-14 MPaG and the second step of conducting hydrocracking at a temperature within the range of 400-480°C at a hydrogen partial pressure of 2-18 MPaG.

Further, the present invention discloses a method of hydrocracking the heavy oils and the like, wherein in the first and second steps, the concentration of the catalyst is 6-40 wt.% of the oil or oil having been treated by heating.

Also, use of the catalyst to hydrocrack~~ing~~ heavy oils is provided.

Please amend the paragraph beginning on page 10, line 23, and ending on page 11, line 9 as follows.

Next, an embodiment of the present invention will be described in detail~~s~~. As methods of producing, from brown coal, active carbon for hydrocracking of heavy oils having specific properties according to the present invention (which will be referred to simply as "the active carbon having specific properties" hereinafter), a method of activation by using a rotary kiln or a fluidized bed is generally known. Here, as a representative example, a method in which the brown coal is activated by using a commercially available rotary

kiln and by the method using steam or mixed fluids of steam and air will be described. However, mixed fluids of steam, air and carbon dioxide (which will be referred to as "oxidative gas") may optionally be used.

Please amend the paragraphs beginning on page 11, line 25, and ending on page 13, line 3 as follows.

Next, in the temperature-programming process, the temperature is raised at a rate of 10°C/minute until the temperature reaches a predetermined value. When the temperature has reached the predetermined ~~one~~value, it is maintained for a predetermined time. Here, the predetermined temperature is within the range of 700 to 1000°C. The predetermined time means a time counted after the temperature ~~having~~has reached the predetermined temperature and is selected from 3 hours to 0 hour. The fixed carbon decreasing rate, which is defined by the formula below, is determined according to the combination of the total amount of the fluid activators and the activation temperature. These definitions are common in the fluid activators described below, as well.

Second, in a case in which mixed fluids of steam and air ~~is~~are used as the fluid activator, steam may be flowed at a flow rate of 3.5-12g/min with respect to 190g of the charged brown coal. In a case in which air is used as the fluid activator, it is preferable that no more than 4 vol.% of oxygen is contained in the mixed fluids, and the predetermined temperature is selected from the range of 500 to 700°C and the predetermined time is selected from the range of 120 to 10 minutes. When the oxygen content exceeds 4 vol.%, the volume proportion of mesopores whose pore diameter is within the range of 2

to 50 nanometers is decreased in the obtained active carbon and the volume proportion of macropores is increased, which should be avoided. In a case in which an oxidative gas is used as the fluid activator, it is also preferable that no more than 4 vol.% of oxygen is contained in the oxidative gas, and the predetermined temperature is selected from the range of 500 to 700°C and the predetermined time is selected from the range of 120 to 10 minutes.

Please amend the paragraphs beginning on page 15, line 1, and ending on page 17, line 3 as follows.

As the method by which iron is impregnated on the active carbon produced by the aforementioned method, the generally known impregnation-evaporation to dryness method was employed ~~with~~using an aqueous solution of iron compounds. Preferably, the active carbon having the aforementioned properties is soaked in an aqueous solution of iron nitrate and then subjected to evaporation to dryness. After that, the nitrate is thermally decomposed in <u>a</u> nitrogen atmosphere, thereby obtaining the active carbon catalyst with iron carried thereon.

In general, catalysts used for hydrocracking of heavy oils have to be subjected to pre-sulfurization of the catalyst metals in advance, then activated, prior to use of the catalysts. However, the active carbon catalyst with iron carried thereon which is produced in the aforementioned manner, has an advantage that the activation is not required because the catalyst reacts with the sulfur contained in the heavy oils and is sulfurized during the hydrocracking of the heavy oils.

In the present invention, the amount of iron to be carried on the active carbon is preferably 1 to 20 wt.% <u>with respect</u> to the active carbon. When the amount exceeds 20 wt.%, the dispersion of iron carried on the active carbon is deteriorated, resulting in insufficient exhibition of iron sulfide as an activation species after being reduced in the reaction site. In hydrocracking, the reaction of hydrogenation could be supplementarily adjusted by pressure, but in such a case, the pressure may exceed the economical range in terms of equipment design. Therefore, the most preferable amount of iron to be carried on the catalyst needs to be provided.

On the other hand, when the amount of the iron is no more than 1 wt.%, as described below, the hydrogenation effect of iron with respect to hydrocarbon radicals adsorbed in the active carbon is insufficient, and in the case of extraheavy oils, generation of coke is increased<u>,</u> especially due to polycondensation.

Next, a reaction test with respect to the first step and the second step of the present invention will be described.

In the reaction test, a flow reaction device was used in which the first and second steps were carried out by changing the amount of iron carried on the active carbon and the concentration of the iron-carrying active carbon.

In the process of cracking heavy oils, bonding between hydrocarbons having a relatively large molecular weight is broken and hydrocarbon radicals are generated. These hydrocarbon radicals are quite reactive and cause chain reactions. As a result, on one hand, the reaction in which heavy oils is made lighter due to cracking proceeds exceedingly <u>well</u> and generation of gases

increases, thereby reducing the yield of fractions of desired naphtha, keros~~i~~ene, gas oils and the like. On the other hand, the hydrocarbon radicals ~~are bonded~~bond with each other and the polycondensation reaction proceeds as well, eventually producing coke. In cracking extraheavy oils containing a relatively large amount of asphaltene, in particular, these chain reactions can be suppressed by adding hydrogen to the hydrocarbon radicals at timings when the polycondensation reaction predominantly proceeds.

Please amend the paragraph beginning on page 17, line 19, and ending on page 18, line 2 as follows.

In the first process, the active carbon catalyst having iron carried on the active carbon was charged and hydrocracking was carried out, while hydrogen was continually supplied in the conditions described below. A catalyst in which 1 to 20 wt.% of iron was carried on the active carbon was used and the concentration of the catalyst was adjusted within the range of 6 to 40 wt.% with respect to the oil which was present in the reactor. When the concentration exceeds 40 wt.% with respect to the oil, fluidity of the oil extremely deteriorates, which is not practically preferable.

Please amend the paragraph beginning on page 18, line 22, and ending on page 19, line 21 as follows.

A catalyst in which 1 to 20 wt.% of iron was carried on the active carbon was used and the concentration of the catalyst was adjusted within the range of 6 to 40 wt.% to the oil which was present in the reactor. When

the concentration of the catalyst exceeds 40 wt.% with respect to the oil, fluidity of the oil extremely deteriorates, which is not practically preferable. The reaction temperature in the second process is normally selected in the range of 400 to 480°C and preferably in the range of 410 to 450°C. The reaction pressure is preferably selected within the range of 2 to 18 MPaG, and more preferably within the range of 7 to 12 MPaG. In this case, the reaction pressure needs to be provided under the pressure of hydrogen gas.

There is no particular limitation to the type of reaction. Examples of the reaction type include fixed bed, moving bed, suspension bed (or slurry bed) and ebullated bed. Any of these examples may be employed, but a completely-stirred tank reactor such as the suspension bed and the ebullating bed is preferably employed.

The whole amount of the cracked products was filtered by a 5-micron filter, and the obtained residue was subjected to toluene extraction by using a Soxhlet apparatus and vacuum dried for 1 hour under conditions of 8-15 torr and 130°C. The amount of coke produced in the oil was determined as the toluene insoluble amount obtained as a result of weight measurement of the vacuum dried residual.

Please amend the paragraphs beginning on page 20, line 5, and ending on page 22, line 6 as follows.

In particular, with respect to the stability evaluation of the obtained product oil, the spot test method of the Nisseki type was employed. The Nisseki type spot test is a method which was proposed in order to

evaluate the stability of heavy oils for ships commonly used ~~for~~as fuel oil for ships. Stability of the oil is evaluated by ranking the oil in the range of No. 1 to No. 6 according to the amount of sludge contained in the heavy oil. In this index, the larger the rank number, the larger amount of sludge is supposed to be contained in the heavy oil, thereby becoming less stable.

The hydrocracking method of the present invention achieves the following effects in producing light hydrocarbons by hydrocracking heavy oils or (in particular) extraheavy oils of poor quality containing a relatively large amount of asphaltene, residual carbon and the like.

(1) Ni and V as ~~the~~heavy metal contents in the oil can be removed without heavily depending on the hydrocracking rate. The residual carbon decomposition rate and the asphaltene (which is defined as the content insoluble to heptane) decomposition rate can be increased according to the hydrocracking rate of the oil and thus generation of coke can be suppressed when the conversion rate is relatively high. Accordingly, light hydrocarbons containing a relatively large amount of useful intermediate fractions can be produced with a high liquid yield. In addition, the properties of the oil are excellent.

(2) Ni and V as ~~the~~heavy metal contents in the oil can be selectively removed. Accordingly, the present invention can be utilized as the ~~technique of the~~catalyst to be charged in a "guard reactor" which is provided upstream of a desulfurizing process or the like, in order to remove heavy metals from heavy oils or the like.

Examples

The present invention will be further described in ~~details~~ detail by examples. Needless to say, the present invention is not limited to the examples described below.

Preparation Example 1

190 g of Yallourn brown coal char was charged as a raw material into a rotary kiln. Water and vapor content was removed by keeping the material under a flow of steam at a flow rate of 3.5 g/min at 600°C for 1 hour. The activation was carried out at 850°C for 150 minutes. The active carbon "B" prepared in this manner was soaked in an aqueous solution of iron nitrate and then subjected to the evaporation to dryness treatment, so that 10 wt.% of iron, to the amount of the active carbon, was carried on the active carbon. Thereafter, the nitrate-decomposition was carried out in a nitrogen atmosphere at 400°C for 1 hour, obtaining an active carbon "A" in which iron was carried on the active carbon. The properties of the iron-carrying active carbon "A" and those of the active carbon "B" are shown in Table 1.

Please amend the paragraph beginning on page 27, line 7, and ending on page 27, line 11 as follows.

Comparative Example 2

A Middle-Eastern based mixed vacuum-distillation residual oil having properties shown in Table 2 was used as the feedstock. In an autoclave reactor, 5 wt.% of the iron-carrying active carbon "A", whose properties are shown in Table 1, was charged with respect to 100 wt.% of the oil which was present in the reactor to be processed, and the hydrocracking was carried out. The reaction conditions and results are shown in Table 7. According to the results, the amount of produced coke was 10.3 wt.%

while the conversion rate of the fractions whose boiling point was no less than 525°C was 84.1%.

Please amend the paragraphs beginning on page 34, line 2, and ending on page 35, line 3 as follows.

When the aforementioned Examples are compared with the Comparative Examples, it is obvious that Examples 1 and 2 exhibit less amounts of coke generation than Comparative Examples 1 and 2. Accordingly, it is understood that the method of the present invention effectively suppresses generation of coke in hydrocracking.

When the stability of the decomposed oil in Example 3 in which the processing was carried out at two stages according to the present invention is compared, on the basis of the results of the Nisseki-type spot test, with the stability of the cracked oil in Comparative Example 3 in which the processing was carried out at one-stage, Example 3 of two-stage processing got No. 3 while Comparative Example 3 of one-stage processing got No. 4, although Example 3 and Comparative Example 3 both show the same conversion rate. Accordingly, it is understood that Example 3 exhibits a more excellent stability of the cracked oil.

Please amend the paragraph beginning on page 35, line 14, and ending on page 35, line 22 as follows.

In Examples 4-7, the heavy metal (Ni+V) removal rate is significantly high (90-94%, approximately) and the residual carbon content in the produced oil and asphaltene defined as the heptane insoluble content are

removed by decomposition as the conversion rate increases. Also, the softening point of the residual oil having a boiling point no lower than 525°C is stable up to the high conversion rate area and the generation of coke is suppressed. Accordingly, it is understood that the catalysts used in Examples 4-7 are very excellent ones.

Please amend the paragraph beginning on page 37, line 9, and ending on page 37, line 21 as follows.

When the catalyst is used as a catalyst to be charged in "a guard reactor", which is provided upstream of the desulfurization process and the like in order to remove heavy metals in the heavy oils, the conventional catalyst of CoMo/alumina carrier described in the reference, Lillian A. Rankel, Energy & Fuels 1993, 7, 937-942, shows a conversion rate of 50 wt.%, which is suppressed at a relatively low level in order to prevent generation of coke, as shown in Referential Example 2 in Table 6. In addition, the Ni removal rate, the V removal rate and the residual carbon removal rate of Referential Example 2 are low as shown in Table 6. Therefore, as is understood from Example 4, the catalyst of the present invention shows excellent performances.